

AMENDMENT UNDER 37 C.F.R. § 1.111
U.S. Application No.: 09/615,708

REMARKS

In the present amendment, independent claim 12 has been amended to delete the polymer light absorbent having a group represented by formula (IX), from the Markush grouping of polymer light absorbents recited in the claim. Also, the spelling of "atoms" has been corrected. In addition, claim 19 has been amended to depend solely from claim 18. Entry of the amendments is respectfully requested.

Claims 12, 14-22 and 24 are pending in the application. Of these, claims 14-18, 20, 22 and 24 have been withdrawn from consideration.

Response to Section 102(b) Anticipation Rejection over Skoultchi

Claim 12 is rejected under 35 U.S.C. § 102(b) as allegedly being anticipated by Skoultchi (3,575,925).

The Examiner asserts that the polymer compositions of Examples I, III, V and VI of Skoultchi anticipate the anti-reflective coating material composition of Applicants wherein present polymer formulas (XIII) and (VXIV) are considered. In each case, the Examiner says n=0 and m=0 in Applicants' formulas. For present formula (XIII) and Skoultchi Example VI, the Examiner says, A₁ is a substituted naphthyl group (-naphthyl-C(=O)-). For present formula (XIII) and Skoultchi Example I, the Examiner says, A₁ is -phenyl-C(=O)-. For present formula XIII and Skoultchi Example III, A₁ is -phenyl-C(=O)-. For present formula VXIV and Skoultchi Example V, A₂ is -C(=O)-phenyl. For present formula (VXIV), the Examiner says, A₂ is -C(=O)-naphthyl. (Presumably, the Examiner is referring to Skoultchi Example VI in this instance).

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The Examiner asserts that these polymer compositions of Skoultchi are inherently useful as anti-reflective coating materials.

Applicants submit that this rejection should be withdrawn because Skoultchi does not disclose or render obvious the bottom anti-reflective coating material composition of the present invention.

The compounds described in Skoultchi have a different structure from those of the present invention and thereby, clearly have a different function from the compounds of the present invention. The compounds of Skoultchi are photosensitive because they have a carbonyl group as a linkage group between the naphthalene ring and the aromatic ring.

In contrast, the compounds of the present invention have a structure in which the aromatic ring is directly linked to the naphthalene ring, and do not react and do not undergo a chemical change even if exposed to light.

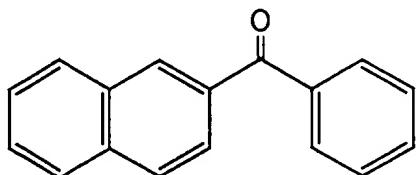
Thus, the compounds for use in the working examples of Skoultchi have a structure in which the aromatic ring is linked to the naphthalene ring via a carbonyl group. In contrast, the compounds of the present invention have a structure in which the aromatic ring is directly linked to the naphthalene ring. Thus, Skoultchi does not constitute a proper basis for rejecting the present claims.

The Examiner cites multiple references related to photosensitive compositions, but a photosensitive composition and a bottom anti-reflective coating material composition are different and have different properties. A photosensitive composition reacts to generate a change such as a solubilization or insolubilization upon an exposure, and then either the exposed areas or

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the unexposed areas are removed by development to form an image. In contrast, a bottom anti-reflective coating material composition can prevent a reflection by absorption of light, and does not essentially require a chemical change in the exposed area. In addition, the photosensitive composition and the bottom anti-reflective coating material composition are a different using mode, e.g., as shown in EP 0159428B1 (especially see the figures). A copy of EP '428 is submitted herewith. Accordingly, it can hardly be said that a composition used as a photosensitive composition is inherently useful as a bottom anti-reflective coating material composition.

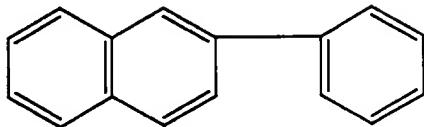
The naphthyl phenyl ketone structure below which is described in the working examples of Skoultchi shows a photosensitive property:



It is known that the aromatic ketone compound as described above shows a photosensitive property. This is described in *PHOTOREACTIVE POLYMERS* (1989) by Arnost Reiser, Chapter 4, pages 113 et seq. submitted herewith. The excited triplet states of the aromatic ketone compound cause a hydrogen abstraction reaction, and therefrom, a radical polymerization reaction is initiated, and as the result, the exposed area hardens to form an image. The naphthyl phenyl ketone structure generates the excited triplet states to react and this is described as Sensitizer No. 6 in Table 1 on page 930 in Wendell L. Dilling et al, *Journal of American Chemical Society*, Vol. 92, No. 4 (170) submitted herewith.

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In contrast, the compound of the present invention in which the aromatic ring is directly linked to the naphthalene ring, as shown,



has no carbonyl group, and does not cause a reaction such as the hydrogen abstraction.

In view of the above, Applicants submit that the § 102(b) rejection of claim 12 over Skoultchi should be reconsidered and withdrawn.

Response to Section 102(e) Anticipation Rejection over Mizutani et al

Claims 12 and 21 are rejected under 35 U.S.C. § 102(e) as allegedly being anticipated by Mizutani et al (6,090,531).

The Examiner asserts that certain polymers disclosed or suggested in Mizutani et al are within the scope of present formula (IX).

As noted above, Applicants have deleted formula (IX) from independent claim 12 in the present Amendment.

Accordingly, the Examiner is respectfully requested to reconsider and withdraw the rejection over Mizutani et al.

Response to Section 102(b) Anticipation Rejection over Teuscher

The Examiner states that claim 12 is rejected under 35 U.S.C. § 102(b) as allegedly being anticipated by Teuscher (3,943,108).

As in the case of Mizutani et al, the Examiner asserts that certain polymers disclosed or suggested in Teuscher et al are within the scope of formula (IX) of present claim 12.

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As noted, Applicants have deleted formula (IX) from claim 12 in the present Amendment.

Accordingly, the Examiner is respectfully requested to reconsider and withdraw the rejection of claim 12 over Teuscher.

Response to Section 102(b) Anticipation Rejection over Unruh et al '103

Claim 12 is rejected under 35 U.S.C. § 102(b) as allegedly being anticipated by Unruh et al (2,716,103).

As in the case of Mizutani et al and Teuscher, the Examiner asserts that certain compositions disclosed or suggested in Unruh et al are within the scope of present formula (IX).

As noted, formula (IX) has been deleted in the present Amendment.

Accordingly, the Examiner is respectfully requested to reconsider and withdraw the rejection of claim 12 over Unruh et al. '103.

Response to Section 102(b) Anticipation Rejection over Unruh et al '097

Claim 12 is rejected under 35 U.S.C. § 102(b) as allegedly being anticipated by Unruh et al (2,716,097).

The Examiner asserts that Unruh et al '097 discloses or suggests polymer compositions within the scope of present formula (IX).

Applicants respectfully submit that this rejection should be reconsidered and withdrawn for the same reason that the preceding three rejections should be reconsidered and withdrawn.

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Claim 24 withdrawn from consideration -- Applicants' Traversal

The Examiner states that newly submitted claim 24 (as now amended) is directed to an invention that is independent or distinct from the invention originally claimed because it relates to the original claims as a process of use of the product. Per the Examiner, the inventions are distinct if the product as claimed can be used in a materially different process. This is shown for the original claims, the Examiner says, by the process of imaging used by Unruh and the process of charge carrier transport used in Teuscher.

The Examiner states that since Applicants have received an Action on the merits for the originally presented invention, this invention has been constructively elected by original presentation for prosecution on the merits. Accordingly, the Examiner says, claim 24 is withdrawn from consideration as being directed to a non-elected invention.

Applicants respectfully traverse for essentially the same reasons as stated at page 3 of the Amendment and Response filed April 9, 2001. As explained there, Applicants respectfully submit that restriction with regard to claim 24 is not warranted, appropriate or fair, because this claim merely recites a method of using the bottom anti-reflective coating material composition of claim 12 to form a resist pattern. Accordingly, Applicants respectfully request that claim 24 be rejoined and considered.

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Response to Objection to Claim 19

The Examiner notes that claim 19 should not have been a choice for election because it is improperly multiply dependent in that it depends on claims 12 and 18 simultaneously.

Claim 19 is objected to as being in improper form because a multiple dependent claim should refer to other claims in the alternative only. Accordingly, claim 19 has not been further treated on the merits.

To overcome the objection to claim 19, Applicants have amended it so that it depends solely from claim 18.

In view of the above, Applicants respectfully submit that claim 19 should be treated on the merits in the next Action.

Claims 14-18 and 20 Withdrawn from Consideration -- Applicants' Response

Claims 14-18 and 20 are withdrawn from further consideration, as being drawn to a non-elected species, there allegedly being no allowable generic or linking claim. The Examiner notes that Applicants timely traversed the restriction (election) requirement.

The Examiner states that Applicants' election with traverse of species A (claim 21) as supported by specification selection of working Example 20 and request to search polymer and second component first is acknowledged. The traversal, the Examiner says, is on the grounds that claims 14-20 would cover or read on claim 21. The Examiner states that this is not found persuasive because claim 12 is the generic linking claim between species A, B and C. Only claim 21, the Examiner says, has the second specified components as elected. Since the broad

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generic claim 12 is rejected, all claims without the component are no longer linked to the elected species.

The Examiner states that the requirement is still deemed proper and is therefore made final.

It appears to Applicants that the Examiner's action of withdrawing claims 14-18 and 20 from further consideration is not proper. MPEP §809.02(c), entitled Action Following Election, states that an Examiner's Action subsequent to an election of species "should include a complete action on the merits of all claims readable on the elected species." In the present case, in addition to claim 21, claims 12, 14, 15, 16, 17, 18, 24, and possibly 19 are readable on the elected species. Therefore, Applicants respectfully request the Examiner to provide an action on the merits of these claims.

Further, Applicants note with due respect that the Examiner is incorrect in stating that the election of species was with traverse.

Response to Section 112 Objection

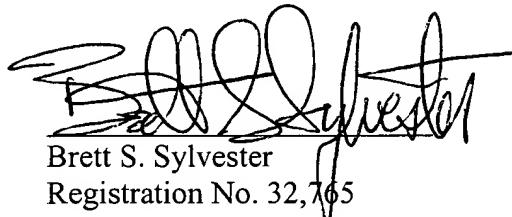
Claim 12 is objected to because in line 16 of claim 12, "toms" should be "atoms". The Examiner requires appropriate correction.

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As noted above, Applicants have corrected this typographical error in claim 12.

Allowance is respectfully requested.

Respectfully submitted,



A handwritten signature in black ink, appearing to read "Brett S. Sylvester".

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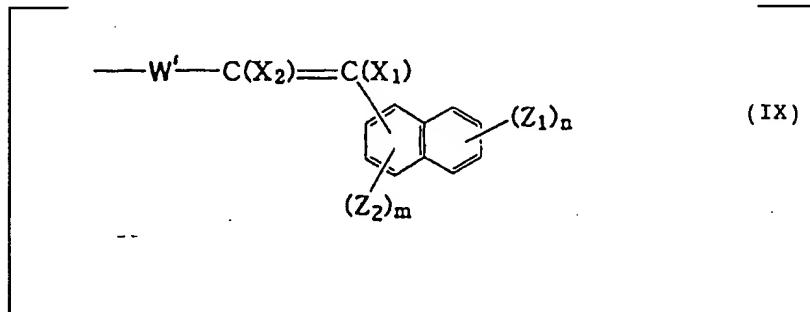
Date: November 21, 2001

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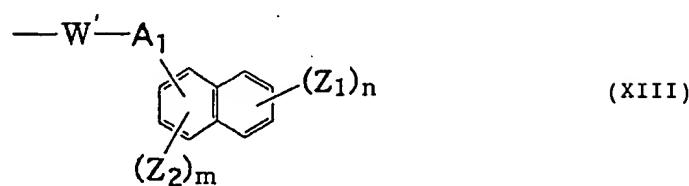
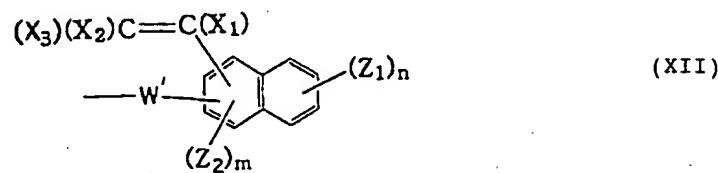
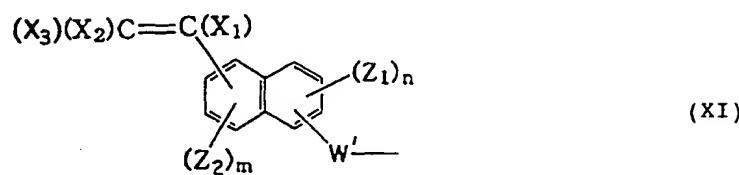
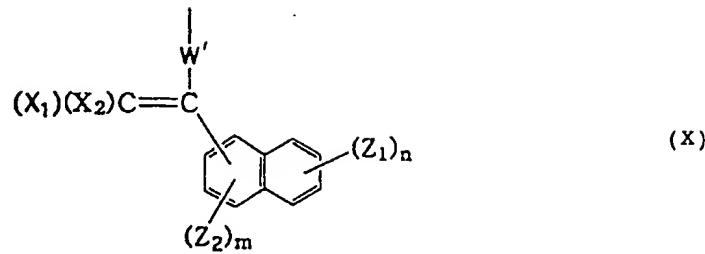
APPENDIX
VERSION WITH MARKINGS TO SHOW CHANGES MADE
IN THE CLAIMS:

The claims are amended as follows:

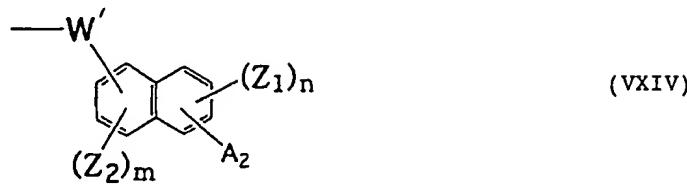
12. A bottom anti-reflective coating material composition comprising a polymer light absorbent having at least one group represented by the following formula [(IX),] (X), (XI), (XII), (XIII), (XIV) or (XV) on the side chain:



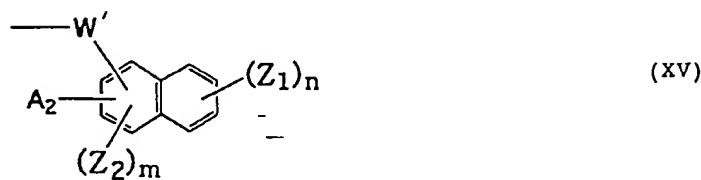
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(XIV)



(XV)

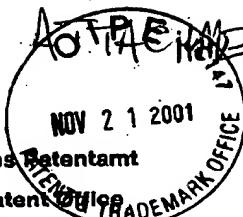
wherein W' represents a divalent linking group, X_1 to X_3 , which may be the same or different, each represents a hydrogen atom, a halogen atom, a cyano group or $-(X_4)_p-R$ wherein R represents an alkyl group having from 1 to 20 carbon atoms, an aryl group having from 6 to 20 carbon [atoms] atoms or an aralkyl group having from 7 to 20 carbon atoms, which may have a substituent, X_4 represents a single bond, $-CO_2-$, $-CONH-$, $-O-$, $-CO-$, an alkylene group having from 2 to 4 carbon atoms or $-SO_2-$, p represents an integer of from 1 to 10, Z_1 and Z_2 , which may be the same or different, each represents an electron donating group, m and n represent an integer of from 0 to 2 and from 0 to 3, respectively, and when m is 2 or m and n each is 2 or 3, the Z_1 groups or the Z_2 groups may be the same or different, A_1 represents a divalent aromatic ring or heteroaromatic ring group having from 5 to 14 carbon atoms, which may have a substituent, and A_2 represents an aromatic ring or heteroaromatic ring group having from 5 to 14 carbon atoms, which may have a substituent.

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19. (Amended) A bottom anti-reflective coating material composition as claimed in claim [12] 18, wherein said polymer light absorbent contains from 2 to 50 wt% of a repeating structural unit represented by formula (XXVII) of claim 18 where B_1 is a group obtained by the reaction of a group represented by $-CONHCH_2OH$, $-CONHCH_2OCH_3$, $-CH_2OCOCH_3$, $-C_6H_4(OH)CH_2OH$, $-C_6H_4(OH)CH_2OCH_3$ or $-CONHC(CH_3)_2CH_2COCH_3$, with formalin.



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Divisional application 87113957 filed on 24.09.87.

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(62) Anti-reflective coating.

(43) Date of publication of application: 30.10.85 Bulletin 85/44

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(62) Designated Contracting States:
 DE FR GB IT NL

(60) References cited:

| | |
|-----------------|-----------------|
| EP-A- 0 087 582 | DE-A- 1 697 597 |
| GB-A- 785 858 | GB-A- 2 085 609 |
| US-A- 4 362 809 | US-A- 4 370 405 |

JOURNAL OF APPLIED PHOTOGRAPHIC ENGINEERING, vol. 7, no. 6, December 1981, pages 184-187, Rochester, N.Y., USA; T. BREWER et al.: "The reduction of the standing-wave effect in positive photoresists"

JOURNAL OF APPLIED PHYSICS, vol. 55, no. 4, February 1984, pages 1110-1115, New York, USA; YI CHINGLIN et al.: "Improvement of linewidth control with antireflective coating in optical lithography"

IBM TECHNICAL DISCLOSURE BULLETIN, vol. 13, no. 1, June 1970, page 38, New York, USA;

H.A. KHOWY et al.: "Anti-Interference phenomena coating"

CHEMICAL ABSTRACTS, vol. 101, no. 16, 15th October 1984, page 642, no. 140939k, Columbus, Ohio, USA; M.P.C. WATTS: "A high-sensitivity two two-layer resist process for use in high resolution optical lithography" & PROC. SPIE, INT. OPT. ENG. 1984, 469 (ADV. RESIST TECHNOLOGY) 2-10

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Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

Description

The present invention relates to a photolithographic resist having a novel anti-reflective coating, and to processes for producing such a photolithographic resist and integrated circuit elements using such a resist, as well as to a novel composition useful in the production of such a photolithographic resist.

The miniaturizing of systems utilizing complex integrated circuits has required that increasingly complex circuitry be imprinted on chips of decreasing size. This reduction in size, or increase in volumetric capacity, has reached the point where the techniques available to the industry have been stretched to the limit of their capabilities. As it is, the yield of the most advanced integrated circuit chips produced by standard techniques is extremely low, of the order of 1%, due to attempts to put more and more capacity into a smaller and smaller volume. At the level of capacity which is being demanded by the industry today, the current photolithographic processes cannot produce a complete, workable structure more than about 1% of the time.

The problem is due to a large extent to the limitations of the photographic process used. At the microscopic level which is required, the layers of chip material, silicon, for example, are not perfectly smooth and flat. Moreover, the uneven topography is of a magnitude approximating that of the wavelength of the light which is used to form the images in the photoresistive material which is applied to the layers of the chip. The light which is used to image the photoresistive material is reflected from the substrate of the chip material, that is, the silicon wafer. This reflection, coupled with the uneven topography, causes an uneven distribution of light in the imageable material and results in a large number of artifacts being produced in the developed image. These artifacts cause a large number of rejects in any semi-conductor structure built by current techniques.

It is apparent that if artifacts can be eliminated or reduced the yield of integrated circuit chips can be increased, resulting in great efficiency and reducing the cost of producing such materials.

Recently there have been a number of attempts to reduce the artifacts caused by reflected light. U.S. Patent No. 4,102,893 discusses one such attempt. Other discussions appear in the IEEE Transactions on Electron Devices, Edition 28, No. 11 of November 1981, pages 1405 to 1410, entitled "Line Width Control and Projection Lithography Using a Multi-Layer Resist Process" by O'Toole, et al. and in "Reduction of the Standing Wave Effect in Positive Photo-Resist," Brewer, et al. In Journal of Applied Photographic Engineering, Vol. 7, No. 6,

Dec. 1981, pages 184 to 188, and "Control of One-Micron Lines In Integrated Circuits," Carlson, et al., Kodak, '80 Interface, October 1980, pages 109 to 113.

We have now discovered an improved photolithographic process for integrated circuits, an improved anti-reflective material for use therein and an integrated circuit chip utilizing such material. The present process uses an anti-reflective coating that eliminates deleterious effects due to internal reflections from wafer surfaces and photoresist surfaces. The material offers better adhesion, greater light absorption, is a thinner, more uniform coating, and has a more controlled development and requires fewer process steps than those previously known. Also, it is compatible with and images with the photoresist, in the integrated circuit manufacturing process. The coating leaves less residue on the integrated circuit wafers after development.

The present invention thus consists in a photolithographic resist comprising a substrate, a photoresist and a light-absorbing imageable anti-reflective coating between said substrate and said photoresist as defined in claim 1.

The invention further consists in a process for preparing the above photolithographic resist, in which the anti-reflective coating is deposited and fixed to the substrate by depositing on the substrate a continuous layer of a solution of said polyimide resin and/or polyimide resin precursor and baking the product to remove said solvent and fix the resin to the substrate, wherein said solvent is a low surface energy solvent.

The invention still further consists in a process for making an integrated circuit element by photolithography in which a pattern is imaged in the photoresist and anti-reflective coating of the above defined resist, the anti-reflective coating imaging with the photoresist, developing and removing the developed image from the photoresist and anti-reflective coating, the imaged anti-reflective coating developing with and being removed with the photoresist, and etching a pattern defined by the imaged anti-reflective coating and photoresist into the substrate to produce said integrated circuit element.

The invention is further illustrated with reference to the accompanying drawings, in which:

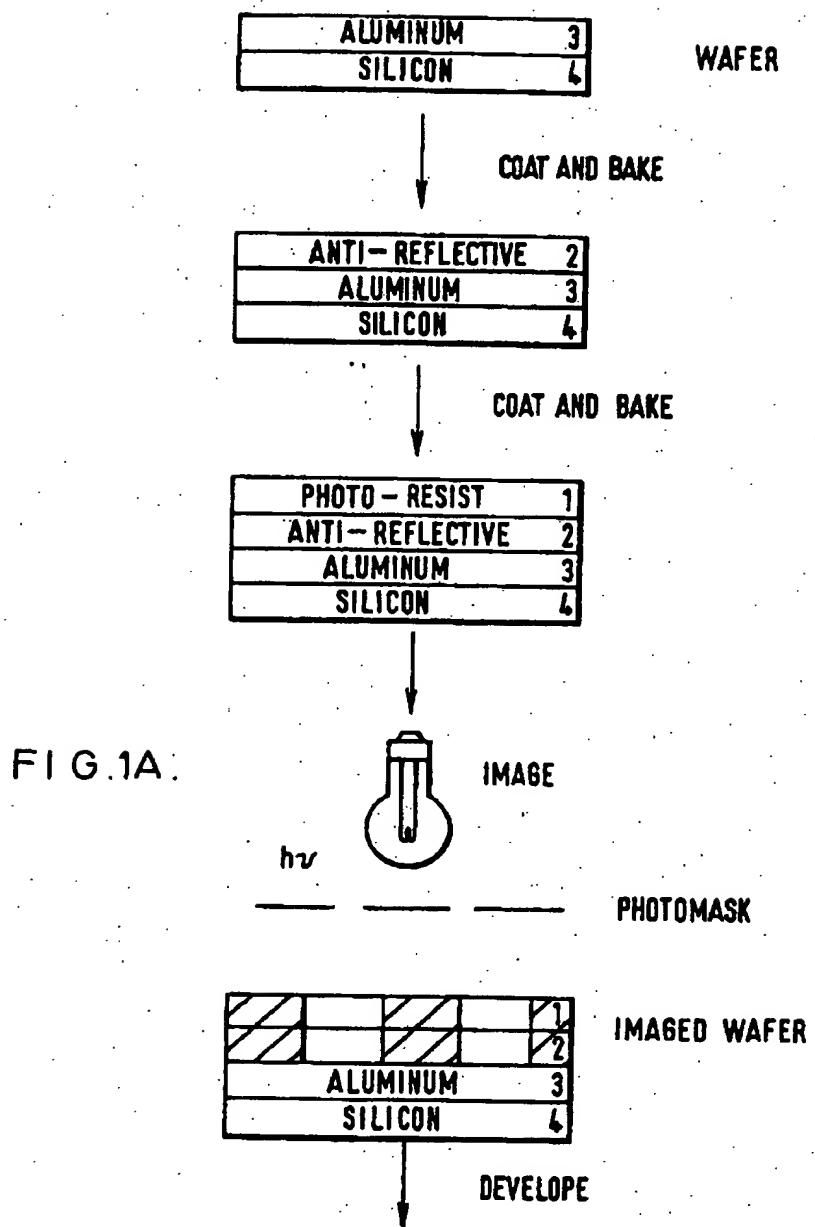
Figure 1 shows a process flow for producing an integrated circuit element using an imageable anti-reflective coating; and

Figure 2 shows modified process steps using a dry etch.

The present invention uses a particular polymer, which is such as to allow the use of common organic solvents having low surface (interfacial) energy, which can produce a firmly bonded, thin and consistent coating on a wafer surface. Suitable

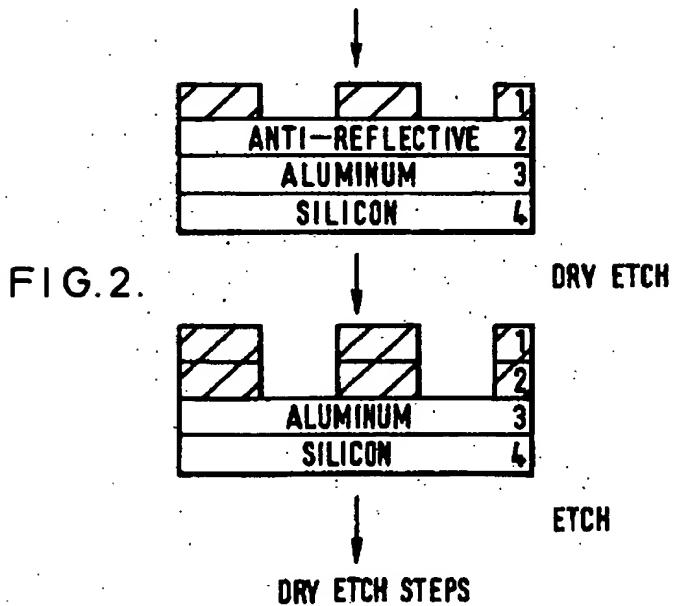
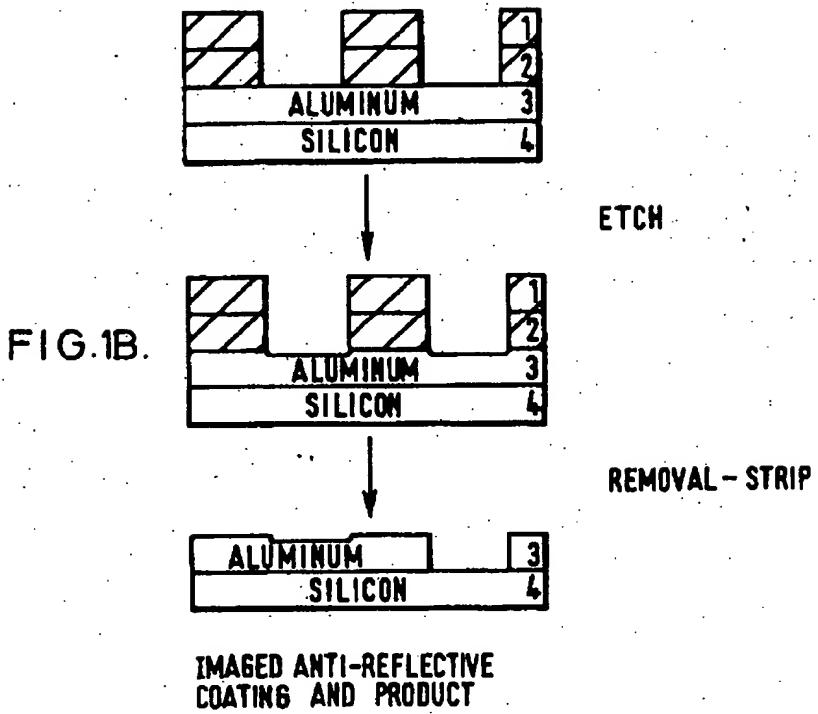
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ATTACHMENT ② - 09/615,708

PHOTOREACTIVE POLYMERS

THE SCIENCE AND TECHNOLOGY OF RESISTS

Amotz Reiser

Institute of Imaging Sciences
Polytechnic University
Brooklyn, New York



WILEY

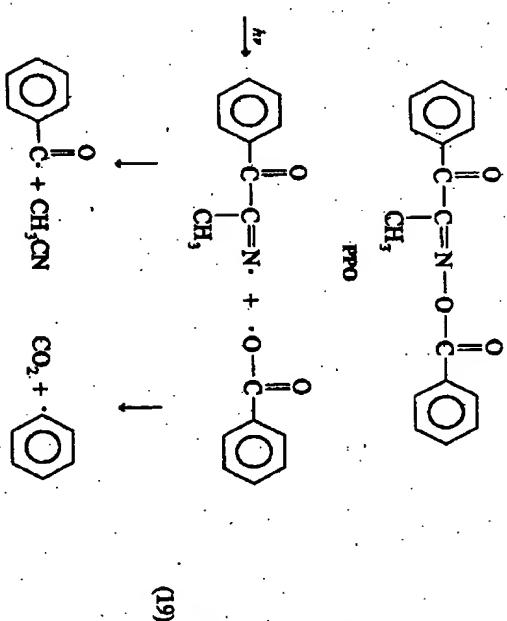
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112 PHOTONITIATED POLYMERIZATION

Ketoxime Esters of Benzoin. The idea of secondary fragmentation, which counters cage recombination and leads eventually to small, highly reactive radicals, is taken one step further in the ketoxime esters first introduced by Delzenne and co-workers [29]. For example, in the photolysis of 1-phenyl-1,2-propanedione-2-O-benzoyloxime (PPO), two volatile fragments are eliminated after primary scission of the N—O bond.



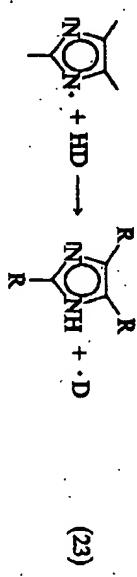
The radical yield of PPO is high ($\phi = 0.9$) and the phenyl radical, the final product of fragmentation, is an aggressive initiating species. In the polymerization of methyl methacrylate, the overall initiating efficiencies of some of these initiators are in the order



Triazines. Another system where multiple fragmentation is brought about by α scission are the symmetrical triazines, which on excitation dissociate into three substituted nitriles [30].

Radicals Generated by Hydrogen Abstraction

Hydrogen abstraction by the excited triplet states of ketones is one of the classic reactions of organic photochemistry. Irradiation of benzophenone, for example, in the hydrogen donor solvent isopropanol leads to the following

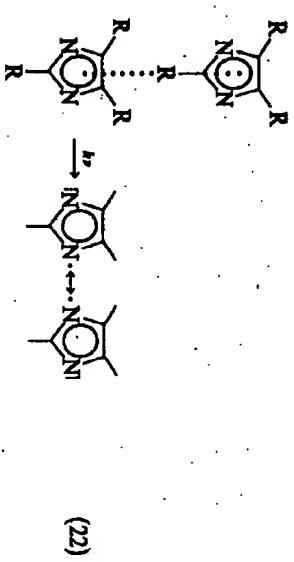


PHOTOGENERATION OF RADICALS 113

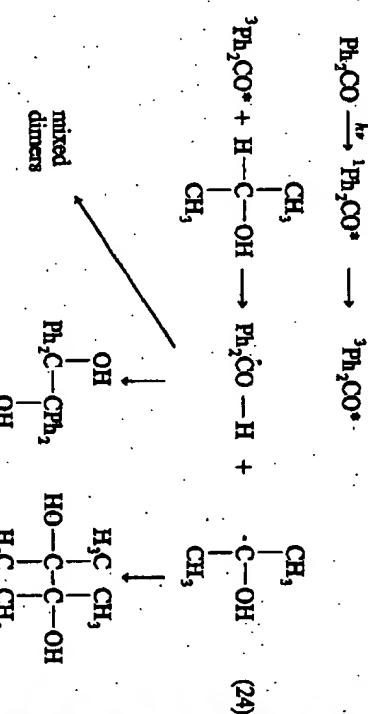
Here the primary photoproducts are not radicals, but they dissociate into radicals in a secondary thermal step.



Biimidazoles. A novel type of initiator based on the idea of incorporating a particularly weak bond into a molecule are the heavily substituted aryl-biimidazoles [31, 32].



processes

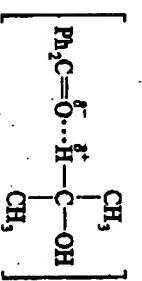


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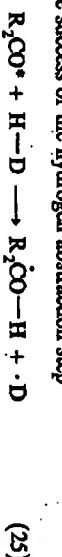
gen abstraction combine into dimers, but in the presence of a reactive monomer they initiate chain polymerization. The species that absorbs radiation and is promoted to an excited state is termed the initiator, the hydrogen donor is the coinitiator.

The triplet excited states of common (aromatic) ketones are known to have $n\pi^*$ configurations, that is, they are formed by promoting an electron from a

nonbonding n orbital on oxygen into an antibonding π^* orbital that is delocalized over the aromatic π system. Charge delocalization produces a partial positive charge on oxygen that may interact with the electron rich C—H bond and lower the energy of the transition state for hydrogen abstraction.

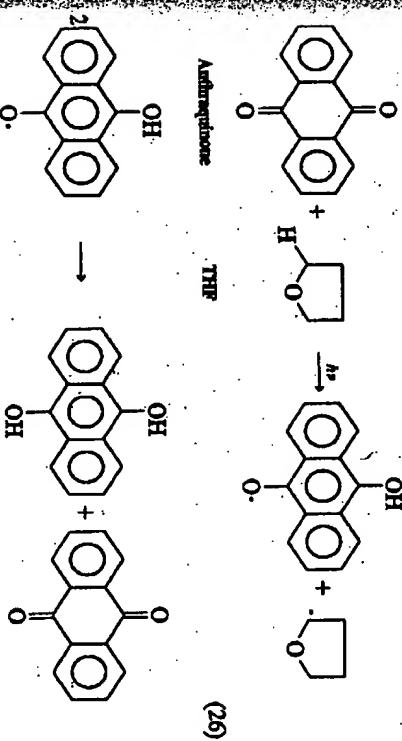


Ketones with $\pi\pi^*$ configurations in the triplet state are less polar and hence less reactive. While $\pi\pi^*$ triplets abstract hydrogen from alcohols and even from tertiary C—H bonds of hydrocarbons, $\pi\pi^*$ triplets are slow to react with alcohols and will only react efficiently with tertiary amines, the strongest



depends on the bond dissociation energies involved and on polar effects in the transition state [34]. Rate constants for the reaction of benzophenone triplet with a range of hydrogen donors are listed in Table 4-2.

| Donor | TABLE 4-2. Rate Constants for the Reaction of Triplets with Various Hydrogen Donors [12] |
|--|---|
| Benzene | |
| Cyclohexane | |
| Methanol | |
| Ethanol | |
| Sopropanol | |
| THF* | |
| <i>n</i> -Nonylmercaptan | |
| Thiophenol | |
| Triethylamine | |
| (Oxygen) | |
| Phenyl dimethylamine | |
| Tetrahydrofuran is abbreviated as THF. | |



Here, the tetrahydrofuryl radical is the principal initiating species [36]. For better solubility, 2-ethylanthraquinone or 2-*tert*-butylanthraquinone are recommended, or in aqueous systems, anthraquinone sulfonate.

Ketone and Tertiary Amines. Benzophenone and tertiary alcohols had been used for some time as initiators when Sander et al. [37] discovered the dramatic enhancement of initiating efficiency brought about in these systems by small additions of tertiary amines. It was found that the effect was caused not only by the good hydrogen donor properties of the alkyl groups in the α position to nitrogen, but also by the ability of the amines to act as electron donors and form **explexes** (excited complexes, see Chapter 3) with the triplet

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for Ruth

Cyclopentadiene to α -Acetoxyacrylonitrile as a Function of Sensitizer Triplet Energy in

Patent L. DULIG; Roger D. Krosinsky, and J. C. Little
Contribution from the Edgar C. Ditten Research Laboratories
The Dow Chemical Company, Midland, Michigan 48640.
Received June 9, 1969

Reaction scheme: Ultraviolet irradiation of 1,3-butadiene and acetoxyacrylonitrile in the presence of triplet sensitizers resulted in 1,3-addition and cycloaddition. 1-*p*-nitro-*p*-nitrophenyl acetate, 1-p-nitro-3-cyano-1,3-butadiene, and trans-1,3-cyclo-2-vinylcyclohexene were cis-1,3-adducts and 4-vinylnitronitriles in high yield at low conversions (ca. 10–20%). At higher conversions increasing amounts of a copolymer were formed. The product distribution as a function of the energy of the lowest triplet energy of the sensitizer was found in general to parallel the product distribution in the dimerization of butadiene and propylene studied by Almstrand and coworkers.¹ Possible reasons for the variation which was observed are discussed.

The photochemical cycloaddition of conjugated dienes to other olefins to give cyclooctene derivatives and other cyclic products is a well-established type reaction and has considerable synthetic utility.¹ We have examined in some detail the photoisomerization² and cycloadditions³ of 1,3-butadiene (1), acryrene (2), α -acetoxyacrylonitrile (3), and cyclopentadiene (4) to a variety of olefins 1 and 2.

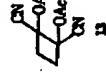
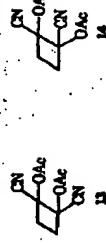
•

The cyclobutane cross-adducts formed.

The cyclobutane cross-adducts 3 and 4 were identified in these cases, and in migration curvatures (22% in the case of the semistar) a 1.3:1 copolymer of 1 and 2 formed.

10.^a The mass spectrum showed a molecular ion peak, m/e 190, and ion peaks for the losses of CH_4 , m/e 175; CO or C_2H_4 , m/e 162; C_2H_7 or CH_3CO , m/e 147;

Irradiation of the nitrile 2 in the presence of acetophenone gave a very slow (compared with cross-addition) conversion to two dimeric products, tentatively



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